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(54) Title: TOILET BAR COMPOSITION MADE WITH POLYMERIC LYOTROPIC LIQUID CRYSTALS (57) Abstract A smooth, polymer containing personal cleansing toilet bar made with polymeric lyotropic liquid crystals.		

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TOILET BAR COMPOSITION MADE WITH
POLYMERIC LYOTROPIC LIQUID CRYSTALS

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FIELD OF THE INVENTION

This invention pertains to personal cleansing toilet bars comprising polymeric material and methods of making such bars with polymeric liquid crystals.

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BACKGROUND OF THE INVENTION

"The liquid crystalline state, which is sometimes called the fourth state of matter, exists between the boundaries of the solid phase and the isotropic liquid phase. In this state some of the molecular order characteristics of the solid phase are retained in the liquid state because of the molecular structure and short range intermolecular interaction. This state of matter may be achieved either by heating or by dissolving the compounds having the proper structure. The ability of some compounds to form a liquid crystalline mesophase has been observed nearly a century ago. Since that time many compounds exhibiting liquid crystalline properties have been synthesized." D. Sek: *Structural variations of liquid crystalline polymer macromolecules*; Acta Polymerica 39 (1988) Nr. 11, p.599.

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It is known to use low molecular weight amphiphile liquid crystals in certain cosmetics. (Dahms, *Cosmetics & Toiletries*, Vol. 101, Nov. 1986, pp. 113-115.) It should be noted that low molecular weight organic surface active amphiphile liquid crystals are distinguished from polymeric liquid crystals. The polymers comprise large molecules made up of repeating units while the former are low molecular weight. Physically and chemically, these two subclasses of liquid crystals are different from each other.

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The primary suggested use of polymeric lyotropic liquid crystals is in the fiber textile manufacturing art (U.S. Pat. No. 4,370,168, Kamide et al., issued Jan. 25, 1983). Also, liquid crystal xanthan gum is reported to stabilize an oil-in-water emulsion (Biological Abstract 79:12413, Food Research Institute,

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Norwich, U.K.). However, no specific application is taught in 79:12413.

It is known to add polymeric materials, per se, to toilet bars for a number of reasons. Some are added to reduce soap bar wet seam cracking (Jap. J57105, 6/30/82, Pola). Others are added for skin feel (U.S. Pat. No. 3,761,418, Parran, Jr., issued Sept. 25, 1973). Yet others are added for skin mildness (U.S. Pat. No. 4,673,525, Small et al., issued June 15, 1987).

While the addition of certain polymeric materials to toilet bar formulations has certain value, the value can be offset by costlier processing, or messy bars, or gritty feeling bars. For example, the addition of polymeric materials as solids, gels, or isotropic solutions, results in the following processing difficulties. (1) The toilet bars are usually more gritty when solid polymers are added. (2) Similarly, when a rigid polymeric gel is added, the polymer tends to separate from the rest of the bar formulation and/or becomes clumps or droplets of gel in the resultant solid bar. A rigid gel is a 3-dimensional cross-linked material with no birefringence. Polymers added in forms (1) and (2) are characterized as being macroscopically distributed in the bar matrix. (3) When added to the bar formulation as an isotropic polymeric weak solution, the amount of polymer delivered is either very low or too much solvent is used. The latter results in a messy bar. In conclusion, these three forms of polymer addition present processing difficulties such as extensive evaporation, excessive grinding, excessive milling, microparticulation, etc., and often result in unacceptable bars.

OBJECTS OF THE INVENTION

An object of the present invention is to provide an improved process to microscopically distribute polymers via polymeric liquid crystals in toilet bar formulations.

Another object of the present invention is to provide a process for making non-gritty, polymer-containing toilet bars using a simplified mixing step.

Other objects will become apparent from the detailed description below.

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SUMMARY OF THE INVENTION

The present invention relates to a toilet bar made with surfactant selected from the group consisting of soap and/or synthetic detergents and from about 0.05% to about 20% by weight of polymeric lyotropic liquid crystals.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a process for making toilet bars containing one or more polymers capable of forming liquid crystals by mixing from about 0.05% to about 20% polymeric lyotropic liquid crystals (comprising polymer and solvent) into a toilet bar formulation whereby the polymers and any associated materials are microscopically and efficiently distributed into the toilet bar formulation.

Some major benefits of incorporating the polymers in the form of liquid crystals, as opposed to incorporating the polymers themselves, or solutions of the polymers, are improved processability and/or improved in-use bar feel and improved economy. The polymeric liquid crystals can also be used to improve distribution of other compounds, e.g., skin care ingredients, perfumes, etc., associated therewith in a toilet bar formulation.

As stated above, the toilet bars of this invention, as compared to other toilet bars made with comparable polymeric material added in a different form, consistently exhibit superior bar properties, especially smoother feel during use. While not being bound to any theory, it is theorized that the benefits of this invention are due to microscopic adsorption of the polymer (or liquid crystals comprising said polymer) onto lipids and/or other solids in the toilet bar formulation.

By comparison, polymers in the form of rigid gels and/or solid polymers tend to be macroscopically distributed in bar formulations, which result in a gritty bar. Thus, the use of polymeric lyotropic liquid crystals for incorporating polymers into a toilet bar formulation is clearly superior to such other forms for incorporating polymer into toilet bar formulations. Isotropic liquid solutions of polymers require too much solvent. The removal of excess solvent adds complexity and expense to the process.

Through the use of the process of this invention, effective levels of polymers, etc., are microscopically distributed into a solid toilet bar formulation, thereby avoiding, or reducing, the drawbacks of using isotropic solutions, solid polymers, or rigid gels. Thus, the present invention provides an improved process for adding polymers that will form polymeric liquid crystals to a toilet bar formulation which avoids excessive evaporation or excessive grinding, milling and/or plodding. Again, only simple mixing is required.

10 Liquid Crystals

In the literature, liquid crystals are also referred to as anisotropic fluids or mesophases. Those terms are used interchangeably. The term "liquid crystals" as used herein means "polymeric lyotropic liquid crystals" unless otherwise specified. The term "lyotropic" means a liquid crystalline system containing a solvent. This type of liquid crystal is distinguished in the art from thermotropic, heat, and magnetically induced liquid crystals. Suitable polymers can have either a non-amphiphilic or an amphiphilic structure. However, these liquid crystals are distinguished from thermotropic liquid crystalline polymers as disclosed in U.S. Pat. No. 4,812,548, Sagane et al., issued Mar. 14, 1989.

A general description of the phase behavior of a soluble polymer in a solvent is as follows: (I) The polymer dissolves in the solvent to form an isotropic polymeric solution. (II) When the concentration of the polymer increases, a mixture of polymeric isotropic solution + liquid crystals is formed. (III) When the level of the polymer increases further and the required mixing is applied, a homogeneous single-phase liquid crystal range is induced. (IV) When even more polymer is present, a mixture of liquid crystals and crystalline polymer forms. (V) When extremely large amounts of polymer are present a crystalline and/or partially crystalline phase are present.

It is important to understand that liquid crystals are substances that possess mechanical properties resembling those of fluids yet are capable of transmitting polarized light (birefringence) under static conditions. In some cases they may show Bragg

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reflections characteristic of a well-defined molecular spacing. They have high degrees of orientational order and chain extensions.

5 Polymeric lyotropic liquid crystals are subdivided into three subclasses: I. nematic, II. cholesteric, and III. smectic, which are optically anisotropic. See J.H. Wendorff, in *"Scattering in Liquid Crystalline Polymer Systems in Liquid Crystalline Order in Polymers,"* A. Blumstein (ed.), Academic Press, Chapter 1 (1978), incorporated herein by reference.

10 I. In the nematic liquid crystalline phase the centers of gravity of the polymeric particles are arranged at random, consequently no positional long range order exists. Within volume elements of a macroscopic sample, the axes of all particles are oriented in a specific direction. Near the smectic-nematic
15 transition temperature, there may be an additional ordering (positional order).

II. The cholesteric liquid crystalline phase is often thought of as a modification of a nematic phase, since its molecular structure is assumed to be similar to the latter. No
20 positional order but only an orientational order exists in the cholesteric phase. In contrast, however, to the nematic phase, the cholesteric phase is characterized by the fact that the direction of the long axes of the molecules change continuously within the sample. This leads to a twist about an axis per-
25 pendicular to the long axes of the molecules. If the pitch of the helical structure agrees with the wavelength of the visible light, selective reflection of monochromatic light can be observed. This effect leads to the iridescent colors often observed in cholesteric phases.

30 III. In the smectic phases the centers of gravity of the elongated molecules are arranged in equidistant planes and smectic layers are formed. The planes are allowed to move perpendicularly to the layer normal and within the layers different arrangements of the molecules are possible. The long axes of the molecules can
35 be parallel to the layer normal or tilted with respect to it. A two-dimensional short range order or a two-dimensional long range

order can exist within the smectic layers. The smectic modifications are labeled according to the arrangement of the particles within the layers.

5 The light microscopy of liquid crystals is described in *The Microscopy of Liquid Crystals*, Norman Hartshorne, Microscopy Publications, Ltd., Chicago, Illinois, U.S.A., 1974, incorporated herein by reference. This reference book discusses birefringence, which occurs in general for mesomorphic states, and methods for microscopic observation and evaluation in Chapter 1, pp. 1-20, and
10 specifically discusses cholesteric mesophase (liquid crystal) systems in Chapter 6, pp. 79-90, both cited sections being incorporated by reference herein. Observation of birefringence is a preferred method for determining occurrence of liquid crystals. Birefringence textures are observed from thin liquid crystal films
15 between glass slides or from thin slices of a material under the polarizing microscope.

I. In thin film samples of a nematic liquid crystalline material, one observes dark flexible filaments under the optical microscope. These are caused by lines of singularities in the
20 molecular alignment. The term "black filaments" is used for this texture. A characteristic texture of the nematic phase is the "Schlieren texture," which is caused by a nonhomogeneous orientation of the particles of the material. One observes dark brushes that start from point defects. A nematic marbled texture
25 consists substantially of a great number of nearly homogeneous regions with different orientation of the optical axes. In a homeotropic texture, the field of view under the polarizing microscope is black in ideal cases. The optical axes and, consequently, the long axes of the molecules are oriented perpendicular to the plane of the thin films. The optical axes of the
30 molecules are oriented parallel to the plane of the film if the samples exhibit the homogeneous texture. Under the microscope one observes large homogeneous birefringent regions. Preferred are the cholesteric liquid crystals.

35 II. The most characteristic texture of the cholesteric phase is the "planar" texture, which is also called the "Grandjean" texture. It is characterized by the existence of a cholesteric

single crystal where the direction of the helical axis is perpendicular to the plane of the film. Bragg reflection of light occurs on planes with equal direction of the long axes of the molecules, resulting in the observation of iridescent colors. The pitch of the helical structure, which determines the optical properties of the phase, can be influenced by temperature, additives, or external forces.

Just below the clearing point one may observe a texture, in which the helical axis is parallel to the plane of the cholesteric film. One can directly observe the pitch of the helix, provided that it is large enough to be resolved. This texture has been referred to as "fingerprint" texture. In thicker samples the "focal conic" texture is usually obtained. Characteristic of this texture is the occurrence of an arrangement of fine dark lines. The lines form ellipses and hyperbolas or parts of ellipses and hyperbolas. The specific pattern is caused by the existence of a lamellar structure that can be deformed in such a way that the distance between the lamellar planes stays constant. In the case of the cholesteric phase the lamellar structure is due to the helical structure; it is thus a supermolecular structure.

III. Certain smectic (A and C) modifications also exhibit a focal conic texture. The lamellar structure is due to the smectic layers, thus it is a molecular structure. Focal conic textures can differ in their appearance. One distinguishes the fan-shaped, the broken fan-shaped, and the polygon textures. No focal conic textures are expected for one smectic (B) modification since the layers cannot be deformed. The smectic (C) modification can exhibit a Schlieren texture since the amount of the tilt of the long axes of the molecules is fixed at fixed temperatures, whereas the direction of the tilt may still vary.

The smectic (B) modification and also the other modifications can show a "mosaic" texture, where homogeneous regions with nonregular boundaries are observed under the polarizing microscope. The optical axes of all particles within one region are parallel; different regions have different orientations. The optical pattern agrees with that described earlier. Homeotropic and homogeneous textures are also observed for smectic phases.

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Focusing on the polymeric lyotropic liquid crystals of the present invention, in general, they are prepared by mixing the polymer with a suitable amount of a suitable solvent. When within the critical concentration and temperature ranges, the mixture
5 forms lyotropic liquid crystals. The polymeric liquid crystalline phase flows under shear and is characterized by a viscosity that is significantly different from the viscosity of its isotropic solution phase. In other words, for some polymers, as the concentration increases, their viscosities increase until they reach
10 viscosity peaks. Then their viscosities decrease dramatically with further increases of their concentrations. The presence of such viscosity peaks signifies the onset of, or the presence of, a polymeric lyotropic liquid crystalline order. Hence, liquid crystals are distinguishable from polymeric systems which are
15 isotropic solutions, pure solids, simple mixtures of solids and liquids and rigid isotropic polymeric gels. Rigid gels do not flow under shear like liquid crystals. Also, when viewed with a polarized light microscope, liquid crystals show birefringence, whereas when isotropic solutions and rigid gels are viewed under
20 polarized light, both show dark fields.

The formation of the liquid crystal state is accelerated by agitation and therefore agitation is preferred. Mixing can be performed either by hand or by mechanical equipment, e.g., an electric dough kneader. A simple empirical technique can be used
25 to determine the onset of liquid crystals for a particular polymer/solvent system.

Again, the formation of polymeric lyotropic liquid crystals is dependent upon a variety of factors. They include the specific polymer and solvent mix, the temperature, the concentration of the
30 polymer in the solvent, etc. Some polymers which form liquid crystals, such as peptides, have rigid backbones; others such as polysaccharides have semi-rigid backbones, and yet other polymers which also form liquid crystals, e.g., block copolymers, have flexible backbones. See, for example, P. Weigel et al., incorporated herein by reference above, and F. Fried and P. Sixou,
35 "Lyotropic Mesophases of Hydroxypropylcellulose in Pure Acetic Acid, in Water, and in Mixed Solvents," *J. of Polymer Science &*

Polymer Chemistry Edition, Vol. 22, 239-247 (John Wiley & Sons, Inc., 1984).

The determination of the liquid crystal phase begins with the selection of the polymer. A polymer, in general, is selected based upon what its role is in the toilet bar formulation. If it is one of the classes of polymers described hereinbefore that will tend to form a liquid crystal phase, then a suitable solvent that is compatible with the toilet bar formulation is selected that is also suitable for making a liquid crystal. A series of concentrations of the selected polymer in the selected solvent are prepared. The domain of the liquid crystal is readily determined by either viscosity measurements and/or polarized light or other techniques as described hereinbefore. The particular temperature range is determined to a great extent by the temperature range that is feasible in the process used to form the toilet bar. The polymer concentration series described hereinbefore, is run of both the top and the bottom of the temperature range set by the toilet bar process. The concentration within the liquid crystal domain and the temperature are selected based upon both convenience in preparation of the liquid crystal phase and the toilet bar. There is only a limited amount of simple experimentation required to determine the limits within which liquid crystals can be formed for a given polymer/solvent combination.

As discussed in detail hereinbefore, liquid crystal formation for any particular polymer and solvent combination is readily identified using one or more of several identification techniques. The onset of liquid crystal formation and the occurrence of a substantially one-phase liquid crystal state for a particular polymer and solvent system can be identified by: (1) visual observation with the naked eye, (2) birefringent optical activity observed by light microscopy; and/or (3) measurement of the polymer/solvent system NMR spectra.

The single phase is a preferred form to mix into a toilet bar formulation as discussed hereinafter. As discussed hereinbefore, a single-phase polymeric liquid crystal composition is distinguished from an isotropic solution, a solid crystalline polymer or a rigid gel containing polymer and solvent. However, liquid

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crystals mixed with some isotropic solution or some gel can be used. Again, the formation of liquid crystal phase is dependent upon several empirical factors. The selection of polymeric/-solvent system, the concentration, agitation level and the temperature are some of those factors.

A. The Polymer

Any polymer useful in, and/or compatible with, personal cleansing toilet bars and which forms lyotropic liquid crystals can be used. Classes of polymers that contain materials capable of forming lyotropic liquid crystals include: polypeptides, polysaccharides, block-copolymers, polysiloxanes, and mixtures thereof. The liquid crystals of the individual polymers must be compatible with other variables, e.g., concentration, the solvent, temperature, etc. While not being bound to any theory, suitable polymers which form liquid crystals can have both polar and nonpolar groups. However, non-amphiphilic rigid and semi-rigid rod polymers do not have both polar and nonpolar groups. Only amphiphilic polymers, such as block copolymers and polysurfactants have both polar and nonpolar groups. Examples of nonpolar (lyophilic, hydrophobic, oleophilic) groups are straight or branched; saturated or unsaturated; cyclic or aromatic: hydrocarbon, polyoxypropylene, polysiloxane, and fluorocarbon chains. Examples of polar (lyophobic, hydrophilic, oleophobic) groups are: -COOM, -OH; -NH₂; -CONR₂; -SH; -SO₃M; etc.; wherein M can be, for example, H alkali metal, e.g., Na, K, etc., or other compatible cation. The groups can be located in the polymeric unit, either centrally or terminally, or both.

Suitable polymers are at least partially soluble in the solvent system described hereinafter. As used herein, "at least partially soluble" means that the polymer is sufficiently soluble in the solvent system to form lyotropic liquid crystals. Minimum solubility required will depend upon the particular polymer-solvent system used. E.g., from about 43 grams to about 60 grams of Klucel® E, a hydroxypropyl cellulose, available from Hercules, Inc., forms a single-phase liquid crystalline order in 100 ml of water at about 30°C. (See Table 2.) The existence of the lyotropic polymeric liquid crystalline order is readily determined by

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testing for the existence of birefringence. Alternative methods of testing include NMR spectra and/or viscosity profile measurements as described herein and in the literature.

Useful polymers are the cationic, nonionic, amphoteric, and anionic polymers. Preferred liquid crystals are made with cationic, or nonionic polymers, or mixtures thereof. Some preferred polymers have molecular weights (MW) of: from about 500 to about 1,000,000, preferably from about 750 to about 200,000, and more preferably from about 1,000 to about 60,000.

Examples of polypeptides include lipopeptides and glycopeptides. The polymers can be natural or synthetic. U.S. Pat. No. 4,600,526, Gallot et al., issued July 15, 1986, discloses the preparation of lyotropic liquid crystals from lipoproteins, said patent being incorporated herein by reference.

Nonionic polymers include some guar gums, and Pluronic® block copolymers of ethylene oxide - propylene oxide. Examples of suitable block copolymers are set out in Table 1.

TABLE 1Block Copolymers

20	Polystyrene-polybutadiene
	Polystyrene-polybutadiene-polystyrene
	Polybutadiene-polystyrene-polybutadiene
	Polystyrene-polyisoprene
	Polystyrene-polyisoprene-polystyrene
25	Polybutadiene-poly(α -methyl styrene)
	Polybutadiene-poly(vinyl-2-naphtalene)
	Polyisoprene-poly(vinyl-2-pyridine)
	Polyisoprene-poly(vinyl-4-pyridine)
	Polyisoprene-poly(methyl methacrylate)
30	Polystyrene-poly(vinyl-2-pyridine)
	Polystyrene-poly(vinyl-4-pyridine)
	Poly(vinyl-2-pyridine) poly(vinyl-4-pyridine)
	Polystyrene-polyisoprene poly(vinyl-2-pyridine)
	Poly(methyl methacrylate) poly(hexyl methacrylate)
35	Polystyrene-poly(ethylene oxide)
	Polybutadiene-poly(ethylene oxide)
	Poly(ethyl methacrylate) poly(ethylene oxide)

TABLE 1 (Continued)

Block Copolymers

	Polybutadiene-poly(benzyl-L-glutamate)
	Polystyrene-poly(benzyl-L-glutamate)
5	Polybutadiene-poly(N ⁵ -hydroxypropyl glutamine)
	Polybutadiene-poly(carbobenzoxy-L-lysine)
	Polystyrene-poly(carbobenzoxy-L-lysine)
	Polybutadiene-poly-L-lysine
	Polystyrene-poly-L-lysine
10	Polysaccharide poly(benzyl-L-glutamate)

Polysaccharides useful for the present invention include a variety of non-cellulosic, cellulosic and cellulose-derivative polymers. Useful polysaccharides include nonionic, anionic and cationic polysaccharides. In addition to cellulose itself, suitable cellulose derivatives include methyl cellulose, ethyl cellulose; ethyl hydroxyethyl cellulose; hydroxypropyl cellulose; sodium carboxymethyl cellulose; hydroxypropylmethyl cellulose; and ethylmethyl cellulose. For a list of polymers see French Patent Publication 2,340,344, Manuel Panar and Oswin Burr Willcox, published Feb. 9, 1977, incorporated herein by reference in its entirety. The particular source of the cellulose for these polysaccharide cellulosic materials is not critical to the invention, and any of the conventional sources can be utilized. These include vegetative plants; including hemp, flax, jute, cotton, and wood. Preferred nonionic polymers include hydroxypropyl cellulose such as that available commercially under the trademarks Klucel E or G marketed by Hercules, Inc., Wilmington, Delaware 19899, and certain guar gum derivatives made by Hi-Tek Polymers of Louisville, Ky.

Polysaccharides that have an average degree of polymerization of at least about 100 anhydroglucose monomer units per polymeric chain are preferred. They must be sufficiently soluble in the solvent to form liquid crystals at the temperature at which soap bars are made. A preferred polysaccharide is hydroxypropyl cellulose which typically has a molecular weight range of from about 2,000 to about 1 million. Other polysaccharides useful for

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the present invention include guar gum, psyllium gum, alginate, carrageenan, xanthan, and locust bean gum. Such polysaccharides can be obtained from the conventional sources, which are well known to those skilled in the art. Non-cellulosic extra-cellular polysaccharides, e.g., xanthan, seaweed extracts, e.g., alginates, carrageenan can also be used.

Many of these and other suitable polysaccharides are described in more detail in *Industrial Gums - Polysaccharides and Their Derivatives*, Roy L. Whistler, editor, Academic Press (New York), 1959, incorporated by reference herein, and also in; P. Weigel et al., "Liquid Crystalline States in Solutions of Cellulose and Cellulose Derivatives," *Acta Polymerica*, Vol. 35, No. 1, 1984, pp. 83-88, also incorporated by reference herein. Some preferred polymers are the guar gum derivatives available from Hi-Tek Polymers, Inc. Some preferred anionic polymers are the sodium alginates (Kelco) and the sodium carboxymethylcellulose polymers available from Hercules. Some preferred cationic polymers are Chitosan and Chitin from Protan, Inc., Redmond, Washington 98052. Specific examples of cationic polysaccharides are JR-125 and JR-400, made by Union Carbide Corporation.

B. The Solvent

The solvents useful for the liquid crystals of the present invention are too numerous to list. They include any suitable solvent or mixture of solvents. Suitable solvents include: water; carboxylic acids, such as oleic acid; alcohols, such as ethanol; polyols, such as propylene glycol and glycerin; perfume and other suitable organic solvents; and mixtures thereof. The most preferred solvents are water and glycerin, and especially water. Other suitable organic solvents include perfume ingredients known in that art. They are just too numerous to list. The selection of one or a mixture is based on aesthetic and polymer compatibility. Suitable perfume solvents are found in U.S. Pat. Nos. 4,145,184, Brain and Cummins, issued Mar. 20, 1979; 4,209,417, Whyte, issued June 24, 1980; 4,515,705, Moeddel, issued May 7, 1985; and 4,152,272, Young, issued May 1, 1979, all of said patents being incorporated herein by reference. Normally, the art recognized perfume compositions are relatively substantive as

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described hereinafter to maximize their odor effect on the skin or hair. However, it is a special advantage of perfume delivery via the perfume/polymer liquid crystal in surfactant/soap compositions. Perfume stability can be enhanced.

5 A substantive perfume is one that contains a sufficient percentage of substantive perfume materials so that when the perfume is used at normal levels in cleansing products, it deposits a desired odor on the skin. In general, the degree of substantivity of a perfume is roughly proportional to the per-
10 centages of substantive perfume material used. Relatively substantive perfumes contain at least about 1%, preferably at least about 10%, substantive perfume materials.

 Substantive perfume materials are those odorous compounds that deposit on the skin or hair via the personal cleansing
15 process and are detectable by people with normal olfactory acuity. Such materials typically have vapor pressures lower than that of the average perfume material. Also, they typically have molecular weights of about 200 or above, and are detectable at levels below those of the average perfume material. However, if used as the
20 sole solvent system, the perfume must be a liquid.

 Perfumes can also be classified according to their volatility, as mentioned hereinbefore. The highly volatile, low boiling, perfume ingredients typically have boiling points of about 250°C or lower. Many of the more moderately volatile perfume ingre-
25 dients are also lost substantially in the washing process. The moderately volatile perfume ingredients are those having boiling points of from about 250°C to about 300°C. The less volatile, high boiling, perfume ingredients referred to hereinbefore are those having boiling points of about 300°C or higher. A signifi-
30 cant portion of even these high boiling perfume ingredients, considered to be skin substantive, is lost during the washing process, and it is desirable to have means to retain more of these ingredients on the dried skin. Many of the perfume ingredients, along with their odor character, and their physical and chemical
35 properties, such as boiling point and molecular weight, are given in "Perfume and Flavor Chemicals (Aroma Chemicals)," Steffen

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Arctander, published by the author, 1969, incorporated herein by reference.

Examples of the highly volatile, low boiling, perfume ingredients are: anethole, benzaldehyde, benzyl acetate, benzyl alcohol, benzyl formate, iso-bornyl acetate, camphene, cis-citral (neral), citronellal, citronellol, citronellyl acetate, paracymene, decanal, dihydrolinalool, dihydromyrcenol, dimethyl phenyl carbinol, eucalyptol, geranial, geraniol, geranyl acetate, geranyl nitrile, cis-3-hexenyl acetate, hydroxycitronellal, d-limonene, linalool, linalool oxide, linalyl acetate, linalyl propionate, methyl anthranilate, alpha-methyl ionone, methyl nonyl acetaldehyde, methyl phenyl carbonyl acetate, laevo-menthyl acetate, menthone, iso-menthone, myrcene, myrcenyl acetate, myrcenol, nerol, neryl acetate, nonyl acetate, phenyl ethyl alcohol, alpha-pinene, beta-pinene, gamma-terpinene, alpha-terpineol, beta-terpineol, terpinyl acetate, and vertenex (para-tertiary-butyl cyclohexyl acetate). Some natural oils also contain large percentages of highly volatile perfume ingredients. For example, lavandin contains as major components: linalool; linalyl acetate; geraniol; and citronellol. Lemon oil and orange terpenes both contain about 95% of d-limonene.

Examples of moderately volatile perfume ingredients are: amyl cinnamic aldehyde, iso-amyl salicylate, beta-caryophyllene, cedrene, cinnamic alcohol, coumarin, dimethyl benzyl carbonyl acetate, ethyl vanillin, eugenol, iso-eugenol, flor acetate, heliotropine, 3-cis-hexenyl salicylate, hexyl salicylate, lilial (para-tertiarybutyl-alpha-methyl hydrocinnamic aldehyde), gamma-methyl ionone, nerolidol, patchouli alcohol, phenyl hexanol, beta-selinene, trichloromethyl phenyl carbonyl acetate, triethyl citrate, vanillin, and veratraldehyde. Cedarwood terpenes are composed mainly of alpha-cedrene, beta-cedrene, and other C₁₅H₂₄ sesquiterpenes.

Examples of the less volatile, high boiling, perfume ingredients are: benzophenone, benzyl salicylate, ethylene brassylate, galaxolide (1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-cyclopenta-gama-2-benzopyran), hexyl cinnamic aldehyde, lyral (4-(4-hydroxy-4-methyl pentyl)-3-cyclohexene-10-carboxaldehyde), methyl

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cedrylone, methyl dihydro jasmonate, methyl-beta-naphthyl ketone, musk indanone, musk ketone, musk tibetene, and phenylethyl phenyl acetate.

5 The perfume/polymeric liquid crystals (perfume/polymer), as described hereinafter, of the high boiling, the moderately volatile, and the low boiling perfume ingredients are stable (a) throughout the mixing of the perfume/polymeric liquid crystals with the toilet bar mixes, (b) during the personal washing and drying of the wet skin, and (c) after drying.

10 Additionally, the solvents utilized to form liquid crystals can optionally carry other soluble additives, including: salts, e.g., sodium chloride and potassium chloride; mono-, di-, and oligo- saccharides, e.g., honey and fructose; perfumes; skin care agents; or other components in amounts safe for human skin treatment.

15 The preferred solvent level of polymeric lyotropic liquid crystals ranges from about 93% to about 40%, preferably from about 80% to about 50%, and more preferably from about 70% to about 60%. The solvent level can, however, be from about 25% to about 35%, so long as it is associated with the polymers in a liquid crystalline state.

20 Moreover, additional solvent can be, and is usually, introduced into the bar formulation separately from the liquid crystals. Typical solid toilet bars contain from about 3% to about 30% of water, based upon the total weight of the toilet bar, more typically, from about 4% to about 25%, but can contain more or less of water. See U.S. Pat. Nos. 4,207,198, to Kenkare, issued June 10, 1980; 4,328,131, to Carson, Jr., et al., issued May 4, 1982; 4,606,838, to Harding, issued Aug. 19, 1986; and 25 4,767,560, to Gervasio, issued Aug. 30, 1988; incorporated herein by reference.

35 The use of liquid crystals in toilet bar manufacturing provides microscopic distribution of the polymer and any associated material while introducing only relatively small amounts of solvent. However, in some cases, larger amounts of solvent are desirable toilet bar components.

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C. Specific Liquid Crystals

Polymers such as JR-125 and JR-400 and water both form liquid crystals. JR-400 and a solvent selected from glycerin or PPG also form liquid crystals. Polymer JR-400 and water also form liquid crystals when a minor amount of a surfactant such as sodium dodecyl sulfate is present. Thus, a minor, but an effective amount of a suitable surfactant, e.g., from about 0.2%-0.6% sodium dodecyl sulfate, can be used to enhance or induce polymeric liquid lyotropic crystal formation for some polymers with certain solvents.

Tables 2 and 3 show some approximate lyotropic liquid crystal single-phase ranges for some exemplary polymers discussed hereinbefore and hereinafter and some solvents. The ranges are illustrative and would vary depending on: (1) the purity of the polymer, (2) its molecular weight distribution, (3) its degree of substitution, (4) the temperature, (5) the type of polymer/solvent mix, and (6) the presence of additives, such as surfactants, salts, etc.

TABLE 2

<u>Nonionic Polymer</u>	<u>Solvent/Temp.</u>	<u>Percent</u>
Sodium Carboxymethylcellulose (D.S. = 1.74)	Water (30°C)	40-60
Hydroxypropyl Cellulose (HPC) (Klucel G TM , Hercules, Inc.) (D.P. = 750) MW ~370,000	Water (30°C)	30-50
Klucel E (HPC) MW ~60,000 to ~80,000	Water (30°C)	43-60

The approximate percentage range of the Liquid Crystal Phase of sodium carboxymethylcellulose in water at 30°C is 40-60% (ratio range about 2:3 to 3:2). The range for Klucel G and water is 30-50% (3:5 to 1:1). See French Patent Publication 2,340,344, Manuel Panar and Oswin Burr Willcox, published Feb. 9, 1977, incorporated herein by reference in its entirety, for more details on liquid crystal ranges.

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TABLE 3

	<u>Polymer</u>	<u>Solvent/Room Temp.</u>	<u>Percent</u>
	JR-400	Glycerin (Room)	10-15
	HPC (Klucel E)	Propylene Glycol	35-60
5	Guar Gum 4413*	Glycerin	35-55
	Guar Gum 4413*	Water	50-75
	HPC (Klucel E)	Water	43-60
	Xanthan (Keltrol F)	Water	10-20
	Guar Gum 4412*	Water	60-75
10	Guar Gum 4412*	Glycerin	20-35
	Guar Gum 4406*	Water	50-65

*Approximate molecular weights for HiTek Polymers 4412, 4413, and 4406 are, respectively, 5,000-12,000; 20,000-38,000; and 31,000-50,000.

15

The approximate liquid crystal phase percentage ranges of the polymer in Table 3 can vary \pm 2-5%.

Keltrol F, xanthan, shown in Table 3, is a polysaccharide made by Kelco, San Diego, California. It has a molecular weight of about 1,000,000. It is in a Liquid Crystal Phase in water at about 10-20%. Klucel E is in a liquid crystal in propylene glycol at 35-60% and in water at 43-60%.

The lyotropic liquid crystals described in the above tables can be microscopically distributed into any suitable toilet bar formulation with minimal mixing or milling. The liquid crystals are mixed well with the other components of the bar formulation with a minimal effort, a marked advantage over the prior art.

D. Toilet Bars

Personal cleansing toilet bars are based on a "surfactant" selected from soaps (alkali metal salts, etc., of fatty acids) and synthetic surfactants and mixtures thereof which are the primary active for cleansing the skin, etc. The term "toilet bar" as used herein means a solid cake comprising soap or synthetic surfactant or mixtures thereof designed and formulated for personal cleansing. The soap and/or synthetic surfactant are present at an effective level, preferably from about 5% to about 95%, more preferably from about 10% to about 90%, more preferably from about

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20% to about 80%, by weight of the bar. Alkali metal soap is a preferred ingredient. An alkali metal (e.g., sodium or potassium) soap or mixture of soaps of fatty acids containing from about 8 to about 24, preferably from about 10 to about 20, more preferably from about 12 to about 18, carbon atoms is preferred. The fatty acid, or acids, used in making the soaps can be obtained from natural sources such as, for instance, plant or animal-derived glycerides (e.g., palm oil, coconut oil, babassu oil, soybean oil, castor oil, whale oil, fish oil, tallow, grease, etc., and mixtures thereof. The fatty acids can also be synthetically prepared (e.g., by oxidation of petroleum stocks by the Fischer-Tropsch process).

The following U.S. patents disclose materials and formulations for toilet bars, and are incorporated herein by reference:

	<u>Pat. No.</u>	<u>Issue Date</u>	<u>Inventor(s)</u>
15	3,761,418	9/1973	Parran, Jr.
	4,234,464	11/1980	Morshauser
	4,061,602	12/1977	Oberstar et al.
	4,472,297	9/1984	Bolich et al.
20	4,491,539	1/1985	Hoskins et al.
	4,540,507	9/1985	Grollier
	4,673,525	6/1987	Small et al.
	4,704,224	11/1987	Saud
	4,812,253	3/1989	Small et al.
25	4,820,447	4/1989	Medcalf et al.

1. Soap

Alkali metal soaps can be made by direct saponification of the fats and oils or by the neutralization of the free fatty acids which are prepared in a separate manufacturing process. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium and potassium tallow and coconut soaps. The term "tallow" is used herein in connection with fatty acid mixtures which typically have an approximate carbon chain length distribution of 2.5% C₁₄, 29% C₁₆, 23% C₁₈, 2% palmitoleic, 41.5% oleic and 3% linoleic. (The first three fatty acids listed are saturated.)

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Other mixtures with similar distributions, such as the fatty acids derived from various animal tallows, are also included within the term tallow. The tallow can also be, and preferably is, hardened (i.e., hydrogenated) to convert part or all of the unsaturated fatty acid moieties to saturated fatty acid moieties. When the terms "coconut oil" and "coconut fatty acid" (CnFA) are used herein, they refer to fatty acid mixtures which typically have an approximate alkyl carbon chain length distribution of about 8% C7, 7% C10, 48% C12, 17% C14, 9% C16, 2% C18, 7% oleic, and 2% linoleic. (The first six fatty acids listed are saturated.) Other sources having similar carbon chain length distribution such as palm kernel oil and babassu kernel oil are included with the terms coconut oil and coconut fatty acid. In the compositions of the present invention, the soap component is preferably either sodium soap or a mixture of sodium and potassium soap wherein the mixture contains no more than about 25% by weight potassium soap.

2. Synthetic Detergents

Some preferred mild synthetic detergent surfactants useful in this invention include alkyl glyceryl ether sulfonate (AGS), anionic acyl sarcosinate, methyl acyl taurate, N-acyl glutamate, alkyl glucoside, acyl isethionate, alkyl sulfosuccinate, alkyl phosphate ester, ethoxylated alkyl phosphate ester, alkyl ether sulfate, methyl glucose ester, protein condensate, mixtures of alkyl ether sulfate and alkyl amine oxide, betaine, sultaine, and mixtures thereof. Any cations present are, typically, sodium, ammonium, potassium, and mixtures thereof. Included in the detergent surfactants are alkyl ether sulfates with 1 to 12 ethoxy groups, especially ammonium and sodium lauryl ether sulfates. The most preferred mild surfactant is sodium AGS. Alkyl chain lengths for these surfactants are C8-C22, typically C10-C18.

Synthetic detergent can be the major surfactant in the toilet bar compositions of the present invention. Preferred types of synthetic detergent are of the anionic or nonionic types. Some soap/synthetic bars of this invention are preferably prepared with mostly soap and up to 20% of a synthetic detergent. If a synthetic detergent is included, a mild one is preferred. A mild

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synthetic surfactant is defined herein as one which does relatively little damage to the barrier function of the stratum corneum. In the primary soap bar formulations, the mild surfactant is preferably used at a level of from about 1% to about 20%,
5 preferably from about 2% to about 15%. In the primary synthetic toilet bar formulation, the levels are reversed.

A preferred toilet bar of this invention comprises from about 5% to about 95%, preferably from about 40% to about 90%, soap or synthetic surfactant. It also contains as an essential ingredient
10 a skin conditioning amount of polymer that has been added as polymeric liquid crystals. The polymers when added in their liquid crystalline state are uniformly distributed on a microscopic level in the soap bar matrix without adversely affecting the smooth feel of the dry or wet bar. They improve the skin feel
15 of the bar when compared to a comparably processed soap bar made with a comparable polymer that is in solid or solid-gel form.

Another preferred bar is prepared with a fatty acid soap and mild surfactant mixture preferably having a ratio of about 2.5:1 to about 37:1, more preferably from about 2.5:1 to about 14:1, and
20 most preferably from about 6.5:1 to about 14:1 (soap:synthetic). Some preferred toilet bars comprising primarily mild synthetic surfactants are disclosed in commonly assigned U.S. Pat. No. 4,673,525, Small et al., supra, and toilet bars which are primarily soap are disclosed in U.S. Pat. No. 4,820,447, Medcalf et
25 al., issued Apr. 11, 1989, both incorporated herein by reference.

3. Other Toilet Bar Ingredients

Insoluble alkaline earth metal soaps such as calcium stearate and magnesium stearate can also be incorporated into compositions of the present invention. These materials are particularly useful
30 in toilet bars in which synthetic detergents are present in that they tend to reduce the relatively high solubility which such bars normally have. These alkaline earth metal soaps are not included within the term "soap" as otherwise used in this specification. The term "soap" as used herein refers to the alkali metal soaps
35 unless otherwise specified.

A wide variety of other materials can be included in toilet bars. Some are included to enhance the physical properties of the

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bar (hardness, wear rate, resistance to water). Others enhance the in-use properties of the toilet bar (lather characteristics such as volume and texture), and some impact on the impression the bar has on the skin both during washing (bar feel) and afterwards.

5 The toilet bars can contain other components conventionally found in toilet bars. E.g., conventional antibacterial agents can be included in the present compositions at levels of from about 0.1% to about 4%. Typical antibacterial agents which are suitable for use herein are 3,4-di- and 3,4',5-tribromosalicylanilides;
10 4,4'-dichloro-3-(trifluoromethyl)carbanilide; 3,4,4'-trichloro-carbanilide and mixtures of these materials. Conventional nonionic emollients can be included as additional skin conditioning agents in the compositions of the present invention at levels up to about 40%, preferably at levels of from about 1% to about 25%.
15 Such materials include, for example, mineral oils, paraffin wax having a melting point of from about 100°F, fatty sorbitan esters (see U.S. Pat. No. 3,988,255, Seiden, issued Oct. 26, 1976, incorporated by reference herein), lanolin and lanolin derivatives, esters such as isopropyl myristate and triglycerides such as
20 coconut oil or hydrogenated tallow. Free fatty acid such as coconut fatty acid can be added to the compositions herein to improve the volume and quality (creaminess) of the lather produced by the compositions herein. Conventional perfumes, dyes and pigments, chelating agents, etc., can also be incorporated into
25 compositions of the invention at levels up to about 5%. Perfumes are preferably used at levels of from about 0.5% to 3% and dyes and pigments are preferably used at levels of from about 0.001% to about 0.5%.

30 A preferred soap bar of this invention is also prepared with from about 2% to about 17% moisturizer, preferably one selected from glycerin and free fatty acid or mixtures thereof. The more preferred bar of this invention contains at least about 4% moisturizer.

E. Toilet Bar Preparation

35 The toilet bars of this invention are prepared in any conventional manner. For example, the polymeric lyotropic liquid crystals are added to noodles of a base surfactant and/or soap

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mixture in an amalgamator. Any optionals such as perfumes, dyes, etc., can also be added to the amalgamator. The toilet bar formulation mixture is then be processed in an amalgamator and milled in a conventional manner under conventional conditions. It can then be extruded (plodded) into logs for cutting and stamping into toilet bars.

In one method, the liquid crystals are preformed and then added to a soap noodle mix in a soap mixing step of a conventional soap bar making process. The incorporation of the polymeric liquid crystals into the soap matrix is fast. The polymeric liquid crystals go into the soap mixture readily and the polymer is adsorbed by the the soap and is distributed microscopically uniformly and without polymer chunks. The microscopic distribution of the polymeric liquid crystals into the soap matrix provides a highly acceptable soap bar feel in-use characteristic. The process of the present invention uses from about 0.05% to about 20%, preferably from about 0.1% to about 10%, more preferably from about 0.2% to about 5%, of polymeric liquid crystals by weight of the toilet bar. The goal is to microscopically distribute the polymer in the toilet bar formulation at a level of at least about 0.03%, and preferably from about 0.1% to about 10%, and from about 0.2% to about 8%, and more preferably at a level of from about 1% to about 5% by solid weight of the toilet bar formulation. The liquid crystals can be added at any convenient step of a toilet bar making process.

Toilet Bar Visual and Smoothness Evaluations

In a bar made with polymeric liquid crystals the polymers virtually cannot be visually detected unaided. Additionally, such a bar does not feel gritty or grainy upon in-use evaluation. On a scale of 0 to 10, as described below in detail, the bar score is a 7 or better (higher) in terms of smoothness.

Tactile Hardspecks Test Method - Bar Feel During Washing

Wash the bar to be tested with both hands for 1 minute in a dishpan which is continually overflowing from a stream of 70°F (21°C) tap water. This will remove surface roughness and sharp edges. Revolve the bar in one hand under water in the dishpan for 10 seconds feeling the front, back, and side panels for draggi-

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ness, sandiness, roughness, and/or individual large hardspecks. Grade the bar using the scale shown below.

Continue washing after 1 minute, up to 2-3 minutes, will verify whether any defects are on the surface or throughout the bar. When this longer washing step is used always report the original grade, from 1 minute 10 second grading, with a notation of any change which occurred.

The hands may become insensitive to bar feel after lengthy immersion in 70°F (21°C) water, so the number of bars tested at one time should be limited to 15. After an interval of perhaps 30 minutes, testing can be resumed.

Grading - Tactile Hardspecks and Dragginess

Grade the test bar for hardspecks (specks) or dragginess on the following scale:

15	Speck or Dragginess	
	<u>Grade</u>	<u>Description of Bar Surface</u>
20	10	Perfectly smooth (like CAMAY® bar soap).
	9	Practically smooth or 1 tactile speck per bar.
	8	Barely detectable sandiness, roughness, dragginess, or 2-3 specks.
	7	Slight sandiness, roughness, dragginess, or 4-5 specks.
25	6	Moderate overall sandiness, roughness, dragginess, or 6-10 specks.
	5	Quite noticeable overall sandiness, roughness, dragginess or 10-20 specks.
	4	Pronounced overall sandiness, roughness, or more than 20 specks.
30	3	Pronounced overall coarse sandiness or roughness (like a LAVA® bar).
	2	Extreme overall coarse sandiness or roughness.
35	1	Extreme overall abrasive roughness.

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Reporting and Grading

Report any defects present in the bar and the grade assigned. Usually one type of defect is responsible for downgrading the bar. In the event that two defects are present, assign the bar a grade based on the worst fault only. If a bar has two faults of equal severity, then assign the bar one full grade lower than it would have received if only one of the faults were present.

Test Method - Wet Soak Smear Test 100 mlProducts Tested

10 Regular size bars or bath size bars restamped to same size as regular.

Equipment

Petri dishes, 90 mm inside diameter, 22 mm deep.

Standard plastic perch.

15 Graduated cylinder or dispensing flask.

Rubber spatula. (Rubbermaid plate and bowl scraper).

Steps

1. Weigh the bar and place centrally on plastic perch in a Petri dish. Add 100 ml of distilled water.
- 20 2. Soak 16-20 hours (overnight). Record time duration of soak.
3. Remove bar from the dish, allow to stop dripping, and weigh the bar. Invert on lab bench for judging.
4. Each judge (at least two are recommended) grades bar smear for type and amount on the following scale:
 - 25 10-9 Smear layer firm to light finger pressure; shallow and dry to hard finger pressure.
 - 30 8-7 Smear layer slightly swollen and slightly soft to light pressure; of moderate depth and fairly firm to hard pressure.
 - 6-5 Smear layer slightly swollen or with noticeable amount of clear gel adhering; deeper and soft to finger pressure.
 - 35 4-1 Smear layer badly swollen; wet, deep, and mushy with an objectionable character.
5. After grading, scrape off smear with a rubber spatula and weigh the bar.

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6. Report results as follows:

- A. Bar grade, as determined in 4.
- B. Weight of gel - weight of soaked bar of Step 3
(wet gel) minus weight of scraped bar of
Step 5.
- C. Net loss - weight of original bar (1) minus
(bar loss) weight of scraped bar (5).

Additional data useful on new or experimental samples:

- D. Weight gain - weight of soaked bar of Step 3
minus weight original (1).

Dye Tracer Test for Polymer Distribution

Suitable dyes used to trace polymers incorporated into a toilet bar formulation are, e.g., methylene blue or "Graff C Stain," available from John Hanley and Associates, Appleton, Wisconsin. The following procedure is used, e.g., for cellulosic polymers:

1. Prepare a 0.1% solution of methylene blue in water or propylene glycol;
2. Dip a thin (0.1-0.2 cm) slice of a bar into the solution;
3. Wash the slice with water; and
4. Observe under a microscope (X10) or with naked eye.

Methylene Blue or Graff C dye will color cellulosic based polymers. In bars made with dry powdered added polymer, methylene blue will form blue spots all over the soap and Graff C yellow spots. This reveals aggregates of polymer distributed in the bar on a macroscopic or an aggregate level. On the other hand, substantially no blue or yellow spots are observed in toilet bars made using liquid crystal, which indicates that the polymers are adsorbed to the soap and microscopically distributed in the bars and are essentially free of macroscopically distributed polymer aggregates.

EXAMPLES

The general procedures for making toilet bars are disclosed in commonly assigned U.S. Pat. Nos. 4,704,224, Saud, issued Nov. 3, 1987; 4,673,525, supra; and 4,820,447, Medcalf et al., issued Apr. 11, 1989, both hereby incorporated herein by reference

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in their entirety. The following exemplified toilet bar formulations show improved properties when polymers are added as liquid crystals versus simple dry addition as a polymeric powder or as a preslurry in coconut fatty acids as disclosed in U.S. Pat. No. 4,704,224, supra. The following examples are presented by way of illustration only.

Bars 1-7 are prepared as follows:

Polymer Addition Mixing Step

Soap noodles are conveyed to an amalgamator mixer where 4 parts of the polymer (8.9 parts of polymeric liquid crystals) are introduced, mixed, and plodded with the soap noodles. 1.1 parts of perfume, 0.13 part Na EDTA (sodium ethylenediaminetetraacetate) solution, 0.0 to 0.50 part of color solution, and 0.2-0.5 part TiO₂ are added and mixed. The polymer/soap noodles (generic noodles) are conveyed to plodding. The generic noodles go through three passes through a three-roll soap mill (feed, middle, outfeed rolls) which is used in this step. Efficient milling is needed in this intimate mixing step. This finished soap formula mixture is then plodded into soap noodles and conveyed via a transport plodder to a final milling step. The mixture is plodded, and then stamped into toilet bars. The resulting bars are tested for physical properties, particularly bar feel properties and smear.

Bars 1-3

In Table 4 there are data showing three toilet bars all containing about 4% hydroxypropyl cellulose (HPC) Klucel E polymer. HPC polymer is respectively added dry and preslurried in coconut fatty acids (CnFA) for Comparative Bars 1 and 2. Their smoothness grades are about 4.5 and 6.4, respectively. Bar 2 is representative of a bar made according to U.S. Pat. No. 4,704,224, supra. HPC is added as liquid crystals in Bar 3. The liquid crystals are made by mixing 45% polymer in 55% solvent (water) at 25°C (RT). When viewed with a polarized light microscope under static conditions birefringence is observed. A cholesteric liquid crystalline texture is noted. The smoothness grade of Bar 3, which exemplifies the invention, is an excellent grade of about 9.5 (out of a perfect 10).

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TABLE 4

Bar Feel of HPC Polymer Bar Soaps

<u>Bar Formulas^a</u>	<u>Fresh Bar Feel^b</u>
(1) 80T/20CN/4% Dry Added HPC ^c	4.5
(2) 80T/20CN/4% HPC PreSlurried in CnFA	6.4
(3) 80T/20CN/4% HPC as Liquid Crystals ^d	9.5

^a All formulas are 80% tallow/20% coconut sodium soap with 8% coconut fatty acid, 11% water, 1.1% perfume, preservatives and color.

^b Bar feel grades range from worse to best with grades of 1-10, respectively. Grades below 7.5 are clearly noticeable by the consumer and are less acceptable to a majority of consumers.

^c Klucel E (molecular weight ~60,000) - dry added.

^d Klucel E - HPC liquid crystals made with about 45% HPC in water at room temperature by mixing by hand until formed.

Optical Microscopy Dye Tracer also shows a benefit of adding HPC polymers as liquid crystals. Visible specks of polymer are seen in a Bars 1 and 2. There are virtually no specks seen in Bar 3, indicating microscopic dispersion of the polymer (polymeric liquid crystals) in Bar 3. As stated above, microscopic dispersion of the polymer (liquid crystals) is evidence that there is enhanced polymer adsorption on the soap/surfactant component of the bar formulation.

Bars 4-7

Significant bar feel improvements are achieved when the polymeric liquid crystals are used instead of dry added polymer. Bars 4-7 each contain about 4% nonionic guar gum polymer. Low molecular weight guar gum and low molecular weight derivatized guar gum, supplied by HiTek Polymers, Inc., Louisville, KY 40202, are used. The polymers in Toilet Bars 5 and 7 are added as liquid crystals. The same polymers are respectively added dry to Comparative Bars 4 and 6. The liquid crystals are made by mixing the particular polymer with water at room temperature. See Table 5

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for details. Birefringent optical activity is observed by light microscopy. See Table 5 for the results.

TABLE 5

	Bar Formulas	Fresh	100 ml Smear	
		Bar Feel	Wt. Gel (g)	Bar Smear Grade
5	(4) 80T/20CN/4% Dry Added Guar Gum ^e	6.9	26.9	5.0
	(5) 80T/20CN/4% Guar Gum Liquid Crystals ^f	9.1	19.4	7.8
10	(6) 80T/20CN/4% Dry Added Derivatized Guar Gum ^g	7.3	29.3	4.9
	(7) 80T/20CN/4% Deriva- tized Guar Gum Liquid Crystals ^h	9.3	19.5	7.1
15				

^e Low molecular weight (MW) T-4406 Guar Gum (Galacto-Mamman Blend) having a MW of from about 31,000 to about 60,000.

20 ^f Low MW T-4406 Guar Gum liquid crystals made with 55.5% guar to 44.5% water. About 7.2 parts are used.

^g Low MW derivatized nonionic 4413 Guar Gum having a MW of from about 20,000 to about 38,000.

25 ^h Low MW derivatized 4413 Guar Gum liquid crystal made with 60% guar to 40% water, MW of from about 1,000 to about 10,000. About 6.7 parts are used.

30 There are also improvements in the economy of the bar soaps when the polymers are added as liquid crystals. See the Smear data above. The Smear test is a measure of a bar soap's economy. The bar is soaked in 100 ml of water. In this test, the weight of the soap gel on the bar is measured and the gel quality is graded. The lower the weight gel the better the economy impression of the bar. The higher the smear bar grade the better the economy impression of the bar. See test procedure above for more details.

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TABLE 6

<u>Bar Formulas</u>	<u>Bar Feel</u>	<u>Bar Smear Grade</u>
(1) Soap + Dry HPC ^c	4.5	-
(3) Soap + PLC HPC ^d	9.5	-
(4) Soap + Dry Guar ^e	6.9	5.0
(5) Soap + PLC Guar ^f	9.1	7.8
(6) Soap + Dry Deri. Guar ^g	7.3	4.9
(7) Soap + PLC Deri. Guar ^h	9.3	7.1

10 In Table 6, a summary of comparative studies of bar feel and smear grades is reported for Bars 1 and 3 through 7. Bars 1, 4, and 6 are Comparative Bars. The bars with polymeric liquid crystals (PLC) show: improved polymer distribution; improved bar feel; and improved in-use economy.

15 In conclusion, the incorporation of polymeric liquid crystals in toilet bars permit better (microscopic) distribution of desirable ingredients (e.g., guar polymers, cellulosic polymers, perfume, etc.) into toilet bar formulations. Other materials incorporated into the bar formulation via polymeric liquid
20 crystals exhibit improved properties since microscopic distribution permits better delivery and increased substantivity of the polymer associated materials on the skin.

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Claims:

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1. A smooth personal cleansing toilet bar comprising:
 - (1) a polymer; said polymer being microscopically distributed in said toilet bar via addition as polymeric lyotropic liquid crystals selected from the group consisting of cholesteric, nematic, and smectic polymeric liquid crystals or mixtures thereof; and
 - (2) an effective amount of surfactant selected from the group consisting of: soap, synthetic detergent, and mixtures thereof.
2. The toilet bar of Claim 1 wherein said liquid crystals are cholesteric.
3. The toilet bar of Claim 1 wherein said bar comprises from about 5% to about 95% of said surfactant and from about 0.1% to about 10% of said polymer.
4. The toilet bar of Claim 1 wherein said bar comprises from about 10% to about 90% of said surfactant and from about 0.2% to about 8% of said polymer.
5. The toilet bar of Claim 1 wherein said surfactant is a mixture of (a) fatty acid soap and (b) mild synthetic detergent in a ratio of (a) to (b) of from about 2.5:1 to about 37:1.
6. The toilet bar of Claim 1 wherein said ratio is from about 2.5:1 to about 14:1 and said polymer is present at a level of from about 0.2% to about 8%.
7. The toilet bar of Claim 1 wherein said polymer is so well distributed that it is essentially free of macroscopically distributed polymer aggregates.
8. The toilet bar of Claim 1 wherein said polymer is selected from the group consisting of: polypeptides; polysaccharides; block copolymers; polysiloxanes; and mixtures thereof, and wherein said

5 polymer has an average molecular weight of from about 500 to about 1,000,000.

9. The toilet bar of Claim 1 wherein said polymeric lyotropic liquid crystals are added at a level so that the polymer is present in said bar at a level of from about 1% to about 5% by weight of said toilet bar and wherein said polymer is selected
5 from the group consisting of hydroxypropyl cellulose having a molecular weight of from about 2,000 to about 1,000,000, and guar gum and guar gum derivatives having a molecular weight of from about 1,000 to about 100,000.

10. The toilet bar of Claim 1 wherein said polymeric lyotropic liquid crystal comprises from about 20% to about 50% of the polymer and from about 50% to about 80% of the solvent on a liquid crystal weight basis.

11. The toilet bar of Claim 10 wherein said solvent is selected from the group consisting of water, carboxylic acids, C₁₋₄ mono-hydric alcohols, C₁₋₄ polyols, perfumes, and mixtures thereof.

12. The toilet bar of Claim 11 wherein said polymeric liquid is made with a perfume solvent.

13. The toilet bar of Claim 1 wherein said toilet bar is smoother and more economical than a comparable toilet bar made with solid polymer.

14. A process for preparing a personal cleansing toilet bar comprising the steps of:

- 5 1. forming a polymeric lyotropic liquid crystal composition comprising (a) from about 7% to about 60% of suitable polymer and (b) from about 93% to about 40% of suitable solvent by mixing;
2. uniformly mixing said polymeric lyotropic liquid crystal composition into a toilet bar formulation to essentially

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10 microscopically distribute said polymers; said formulation comprising an effective amount of surfactant selected from soap, synthetic detergent, and mixtures thereof; and wherein said polymeric liquid crystals are added at a level of from about 0.05% to about 20% by weight of the bar formulation; and

15 3. forming shaped, solid toilet bars from said uniform mixture of Step 2.

15. The toilet bar of Claim 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12 or 13 made by the process of Claim 14.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US90/06760

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ³ According to International Patent Classification (IPC) or to both National Classification and IPC INT. CL.(5): C11D 9/22 U.S. CL.: 252/132														
II. FIELDS SEARCHED <div style="text-align: center; margin-top: 10px;">Minimum Documentation Searched ⁴</div> <table style="width: 100%; border: none;"> <tr> <td style="width: 30%; border: none;">Classification System </td> <td style="border: none;">Classification Symbols</td> </tr> <tr> <td style="border: none;">U.S.</td> <td style="border: none;">252/108, 117, 121, 132, 153, DIG. % & DIG. 16</td> </tr> </table> <div style="text-align: center; margin-top: 10px;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁵</div>			Classification System	Classification Symbols	U.S.	252/108, 117, 121, 132, 153, DIG. % & DIG. 16								
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III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴ <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%;">Category ⁶</th> <th style="width: 70%;">Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷</th> <th style="width: 20%;">Relevant to Claim No. ¹⁸</th> </tr> </thead> <tbody> <tr> <td style="text-align: center;">Y</td> <td>US, A, 4,820,447 (MEDCALF, JR., ET AL.) 11 April 1989, column 2, line 65 to column 3, line 6.</td> <td style="text-align: center;">1-15</td> </tr> <tr> <td style="text-align: center;">Y</td> <td>US, A, 4,812,253 (SMALL, ET AL.) 14 March 1989, column 3, lines 18 to 31.</td> <td style="text-align: center;">1-15</td> </tr> <tr> <td style="text-align: center;">Y</td> <td>G. DAHMS, "Properties of O/W Emulsions With Anisotropic Lamellar Phases" Cosmetics & Toiletries, Vol, 101, p. 113-115 November, 1986.</td> <td style="text-align: center;">1-15</td> </tr> </tbody> </table>			Category ⁶	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸	Y	US, A, 4,820,447 (MEDCALF, JR., ET AL.) 11 April 1989, column 2, line 65 to column 3, line 6.	1-15	Y	US, A, 4,812,253 (SMALL, ET AL.) 14 March 1989, column 3, lines 18 to 31.	1-15	Y	G. DAHMS, "Properties of O/W Emulsions With Anisotropic Lamellar Phases" Cosmetics & Toiletries, Vol, 101, p. 113-115 November, 1986.	1-15
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>[*] Special categories of cited documents: ¹⁵</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Δ" document member of the same patent family</p> </div> </div>														
IV. CERTIFICATION <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none;"> Date of the Actual Completion of the International Search ¹ <div style="text-align: center; margin-top: 10px;">31 JANUARY 1991</div> </td> <td style="width: 50%; border: none;"> Date of Mailing of this International Search Report ² <div style="text-align: center; margin-top: 10px;">01 APR 1991</div> </td> </tr> <tr> <td style="width: 50%; border: none;"> International Searching Authority ¹ <div style="text-align: center; margin-top: 10px;">ISA/US</div> </td> <td style="width: 50%; border: none;"> Signature of Authorized Officer <i>Nguyen Ngoc Ho</i> <div style="text-align: center; margin-top: 10px;">JOHN F. McNALLY INTERNATIONAL DIVISION</div> </td> </tr> </table>			Date of the Actual Completion of the International Search ¹ <div style="text-align: center; margin-top: 10px;">31 JANUARY 1991</div>	Date of Mailing of this International Search Report ² <div style="text-align: center; margin-top: 10px;">01 APR 1991</div>	International Searching Authority ¹ <div style="text-align: center; margin-top: 10px;">ISA/US</div>	Signature of Authorized Officer <i>Nguyen Ngoc Ho</i> <div style="text-align: center; margin-top: 10px;">JOHN F. McNALLY INTERNATIONAL DIVISION</div>								
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